

Structure and Magnetism of Eu_2IrD_5

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A powder neutron diffraction study of $\text{Eu}_2^{153}\text{IrD}_5$ has shown it to be isostructural with Sr_2IrD_5 at room temperature. Unlike the latter compound, it does not undergo a deuterium-ordering transition at low temperatures. Magnetic scattering at helium temperatures confirms the suggestion that it becomes ferromagnetic below 20 K with a moment corresponding to that of divalent europium.

Introduction

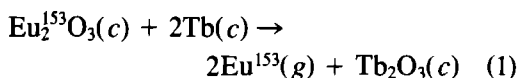
A recent powder neutron diffraction study (1) of the ternary deuteride Sr_2IrD_5 indicated that at room temperature the compound is cubic and that five deuterium atoms randomly occupy the six octahedral sites surrounding the iridium atom. At low temperatures it undergoes a cubic-to-tetragonal phase transformation accompanied by a small lattice distortion and an ordering of the deuterium atoms. X-ray powder results (2) for Eu_2IrH_5 showed that, on the basis of the metal positions, it is isostructural with the corresponding strontium compound. One objective of the present study of Eu_2IrD_5 was to determine the deuterium positions and to ascertain whether an ordering transition takes place at low temperature. Susceptibility measurements

suggest (2) that Eu_2IrH_5 becomes ferromagnetic below 20 K. This investigation addresses this question directly since ordered magnetic structures make characteristic contributions to the diffraction pattern.

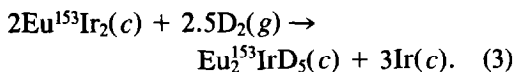
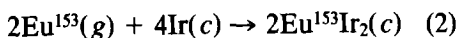
Experimental

Sample Preparation

Powder neutron diffraction studies of Eu compounds require the use of the separated isotope Eu^{153} which, although highly absorbing itself, has less than 7% of the absorption cross section of natural abundance europium. Synthesis of Eu_2IrD_5 posed special problems because only a limited quantity of the isotope was available, and in the form of the oxide. Because of these constraints, a sequence of reactions was chosen that can be represented by



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The final product consists of a mixture of $\text{Eu}_2^{153}\text{IrD}_5$ and Ir metal. The presence of Ir metal is an obvious disadvantage of the method of synthesis, particularly since there is some overlap of diffraction lines. While inconvenient, this presented no fundamental difficulty.

1.4834 g of carefully dried $\text{Eu}_2^{153}\text{O}_3$ were intimately mixed with 1.3985 g of terbium powder and packed into the bottom of a long cylindrical tungsten crucible. A multiple distillation column, made of shredded tungsten foil, was packed on top of the oxide-terbium mixture. In the upper portion of the crucible, 3.2216 g of iridium foil was arranged to expose maximum surface. The crucible was provided with a close-fitting tungsten cap and the entire assembly was sealed, *in vacuo*, in a fused silica tube. A tantalum foil support within the silica tube was used to prevent the crucible from touching the silica wall.

Utilizing rf heating, the temperature of the bottom of the tungsten crucible was raised to approximately 1200°C, at which point the readily observable *exothermic* reaction of the terbium metal and europium oxide takes place, distilling the europium onto the iridium foil, with which it partially reacts. Following the obvious cessation of the reduction process, the unopened silica tube was placed in a resistance-wound tube furnace and heated at 800°C overnight to ensure maximum reaction of the europium metal with the iridium. After cooling, the tube was opened in a helium atmosphere and the EuIr_2 removed. The EuIr_2 , as formed, was brittle and easily pulverized in the inert atmosphere.

The powdered EuIr_2 was reacted with deuterium gas by heating in a fused silica tube that was connected to a deuterium-

purged vacuum system of known volume containing D_2 at 1 atm. At approximately 400°C, a sudden drop in the pressure of the system took place, corresponding to that expected for formation of the hydride.

Note. The selection of terbium metal as the reducing agent instead of the more commonly used lanthanum, was dictated by the results of X-ray fluorescence analysis of various "high purity" rare earth metal batches for contaminants considered undesirable. The terbium powder used in the synthesis was found to contain less than 0.03% (estimated limit of detection) of Eu, Sm, Gd, Yb, and alkaline earth metals, whereas the available lanthanum contained observable quantities of the noted rare earths (0.1%) and alkaline earths (0.02%).

Data Collection

The sample was contained in a flat aluminum cell 0.05 cm thick, which for low temperature experiments was mounted in a variable temperature cryostat capable of reaching He temperatures. Room temperature measurements were made using a conventional two-crystal spectrometer with a Ge(111) monochromator and 20' horizontal soller-slit collimation before the monochromator and before the detector. Data were collected over a range in 2θ from 14 to 65°, using a wavelength of 1.342 Å. High resolution data collection was limited to a small angular range because of the long counting times required for the small, highly absorbent sample. These runs were made using three-crystal geometry, with a Ge(111) monochromator and a pyrolytic graphite(004) analyzer. Horizontal 20' collimation was provided before and after the monochromator, as well as after the sample, and 40' collimation was used between the analyzer and counter.

Room Temperature Structure

All the room temperature peaks, with the exception of several very weak EuO peaks

and Al peaks from the sample holder, could be indexed on the basis of the Eu_2IrD_5 cell, and corresponded to the reflections expected on the basis of an isomorphism with Sr_2IrD_5 . With low resolution, the (200) and (220) reflections of Ir are unresolved from the (400) and (440) peaks of Eu_2IrD_5 . (The lattice constants are 3.839 and 7.580 Å for the two compounds, respectively.) They were separated by calculation, using the mol ratio of 3 : 1 given by the formation reaction (3) above.

Calculated intensities for Eu_2IrD_5 at room temperature were based on the Sr_2IrD_5 structure with space group $Fm\bar{3}m$ (No. 225), Eu in positions $8c$ ($\frac{1}{2}, \frac{1}{2}, \frac{1}{2}; \frac{3}{2}, \frac{3}{2}, \frac{3}{2}$), Ir in $4a$ (0,0,0), and D randomly distributed in sites $24e$ ($\pm x, 0, 0; \pm 0, x, 0; \pm 0, 0, x$). A comparison of low-angle observed and calculated intensities is given in Table I and provides strong support for the assumed isomorphism. Calculated intensities in the table were obtained using a value of the deuterium parameter x equal to 0.22 (determined by best fit in trial calculations), absorption corrections based on a direct transmission measurement, and isotropic thermal parameters taken from Sr_2IrD_5 , assuming $B_{\text{Eu}} = B_{\text{Sr}}$. The computed Ir–D distance is 1.67 Å, which is expected for covalent interaction (3).

Low Temperature Studies

In the case of Sr_2IrD_5 , ordering of D on

TABLE I
THE OBSERVED AND CALCULATED RELATIVE
INTENSITIES OF SEVERAL LOW-ANGLE REFLECTIONS
FOR Eu_2IrD_5 AT ROOM TEMPERATURE

hkl	I_{hkl}/I_{400} (Observed)	I_{hkl}/I_{400} (Calculated) ^a
(111)	67	70
(200)	7	5
(220)	46	45
(400)	100	100
(440)	76	78

^a $x = 0.22$.

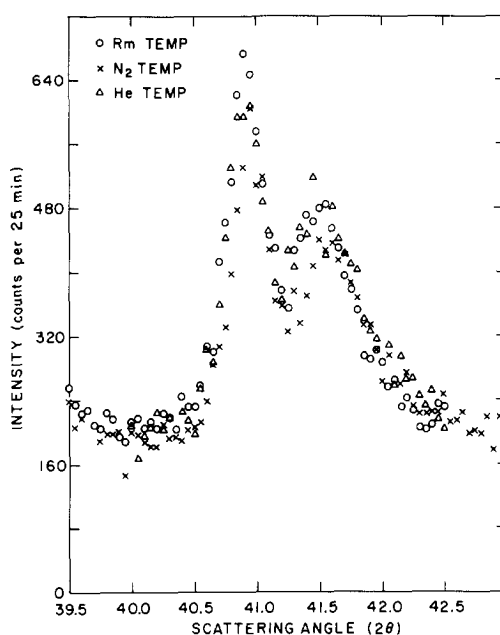


FIG. 1. High resolution scans of the (400) Eu_2IrD_5 reflection at room temperature, 77 K, and 9 K. Peak at 40.9° is the (200) of Ir.

the six sites octahedrally coordinated to Ir was accompanied by a tetragonal distortion, most easily seen in the splitting of the cubic (400) reflection into the (004) and (220) of the tetragonal structure. The possibility of a similar reduction in symmetry for Eu_2IrD_5 was investigated by scanning, at high resolution, the region from 39.5 to 42.5° in 2θ , containing the (400) of Eu_2IrD_5 at 41.5° and the (200) of Ir at 40.9° . The results for room temperature as well as 77 and 9 K are shown in Fig. 1. The data provide *no* evidence for splitting on the scale observed in the case of Sr_2IrD_5 , where the separation of the split components was $\sim 1.5^\circ$ in 2θ .

Magnetic Scattering

At 9 K the intensity of the (111) reflection is essentially unchanged from its room temperature value, whereas the (200) and (220) intensities are increased. These observations are consistent with the suggestion (2)

from susceptibility measurements that Eu_2IrD_5 is ferromagnetic at this temperature, since the Eu moment would contribute scattering to (200) and (220) but not to (111). This follows from the fact that the Eu atom contribution to the structure factor is zero for (111) but nonzero for (200) and (220). Normalizing the increase in intensity to the nuclear scattering, one deduces a moment of $5.0 \mu_B$ from the (200) reflection and $4.6 \mu_B$ independently from the (220) reflection. Assuming a typical Brillouin dependence of the moment, this is equivalent to an ordered moment of $6 \mu_B$ at absolute

zero, with an estimated error of about $1 \mu_B$. This result is reasonably close to the value $7 \mu_B$ expected for divalent Eu and agrees with the effective moment reported (2) in earlier susceptibility measurements.

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